B.Tech Thesis on

Corrosion behavior of Low Carbon Steel in presence of Chlorides, Cyanides, and Sulphates

For partial fulfillment of the requirement for the degree of

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In

Chemical Engineering

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CERTIFICATE

This is to certify that the thesis entitled "**Corrosion behavior of low carbon steel in presence of chlorides, cyanides and Sulphates**" submitted by Abhishek Kumar, Roll No.- 111CH0597, in partial fulfillment of the requirement for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela; is an authentic work carried out by him under my supervision and guidance.

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ABSTRACT

Corrosion is an important phenomena playing a role in day to day life. Every one of us has seen corrosion in one form or another. With the word corrosion the most familiar example which strikes our mind is of rust formation. Corrosion products of iron are commonly known as rust. Among metals and alloy of metals, mils steel is majorly used in all forms of industry and household items. Due to its vast application in multiple fields, it is exposed to varying environment and media. Each and every environment has their own mechanism and tendency to physically and chemically interact with steel. The purpose of this study was to understand the effect of various industrial wastewater components like Chlorides, Sulphates and Cyanides etc. on corrosion rate of mild steel. Weight loss method was used to determine the corrosion rates and point out the concentration which are disastrous to mild steel. Corrosion inhibition is a necessary economic effect. Lots of chemical compounds are known to inhibit corrosion in various environments. In this case Aniline was studied to determine its corrosion inhibition efficiency. It was found that Aniline is highly efficient against chlorides while least efficient against phenols. Aniline was found to be suitable for low temperature range and lost its knack as the temperature was increased. There are other chemicals which can be used to inhibit corrosion. Although question that intrigues mind is, "How these inhibitors can be used at Industrial level to stop large scale corrosions?"

Keywords: - Corrosion, Mild Steel, Inhibition, Aniline

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NOMENCLATURE

IUPAC	International Union of Pure and Applied Chemistry
EPA	Environmental Protection Agency
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray Spectroscopy

CHAPTER 1

Introduction and Literature Survey

Study of corrosion in mild steel is important because of the vast usability of it. Out of all forms of metal mining, 60% accounts for Iron. The major product made from iron is mild steel as it is easy to produce and has a huge demand in market. As per report of National metallurgical Laboratory, Jamshedpur, by year 1991, India was losing 14.1 billion $ every year due to corrosion. If we account it for present year, keeping in mind the industrialization, inflation and other global and local economic factors, this vale can never be less than 50 billion dollars. This is a huge amount of money which can be utilized for other welfare and innovative purposes if saved from corrosion. If proper inhibition methods are developed, Industries can have hassle free operation. This will save their money in form of replacement and operating costs.

Corrosion has been widely studied all around the globe with little success so far for large scale Industrial application. For a particular type of environment it is easy to inhibit corrosion by tweaking the material or the media. It becomes difficult when nature of environment keeps changing. A very simple solution to inhibit corrosion is use of specialized materials, but this can't be economical most of the time due to rarity of special elements. The general solution which can be applied and controlled easily is the tweak in nature of corrosive environment to make it less active. This demanded the study of wastewater and its effect on corrosion of mild steel. Wastewater was found to have various organic and inorganic components. The separate study of these components was done to understand the individual effect of them on mild steel. Further Aniline as an inhibitor was used with wastewater and weight loss experiments were conducted to determine the inhibition efficiency.

1.1. Mild steel

Steel is an alloy of Iron. Alloy is a substance formed by a combination of two or more metals. They are new metal exhibiting the properties of all the metals used in the formation. Among all alloys, Steel is used more than any other. From simple things like cutlery and cookware to heavy machinery, steel is used in almost every field. This high use is due to its strength, durability, and other such favorable properties.

Among various grades of steel, Mild steel is a very popular metal, widely used and one of the cheapest types of steel available. It has its uses in almost every metal application. Mild steel is a low carbon steel and contains less than 1 % carbon, which makes it respond efficiently to magnetization as well as enhances its weldability. Since it's relatively cheaper, mild steel is advisable for major projects requiring vast amounts of steel. Mild steel comparatively lacks the property of structural strength, making it undesirable for building girders or structural beams.

Among all everyday products made from steel, majority of them is made up of mild steel. Due to its strong liking to corrosion, mild steel must be processed through any inhibition method to keep it from rusting. Putting a coat of grease, paint or oil on mild steel enhances its durability against corrosion. Mild Steel is a soft material and is easy to weld. In the same place, high-carbon steels, such as stainless steel, requires the use of specialized welding methods and techniques. Also, electricity flows through mild steel easily without affecting its structural integrity. Mild steel is a variation of hard steels, which makes it considerably less brittle and increases its flexibility. It accounts for the 90 % of steel produced worldwide (Ashby et al., 1992).

1.1.1. Properties of mild steel and Uses

Properties of mild steel and their application in various fields of science and technology.

- The average density of industry grade mild steel is 7861.093 kg/m3. Young's modulus value is approximately close to 210,000 MPa.
- An addition of a moderate amount of carbon introduces properties in this steel different from other types. Carbon atoms occupy in the interstitial sites within the iron lattice, making it stronger and harder. However, the hardness comes at the cost of a reduction in ductility.
- Compared to other different grades of steel available in the market, this type is ideal for welding purposes, as it conducts electric current efficiently without affecting the metal surface.
- Mild steel has ferromagnetic properties, which make it suitable for the manufacture of electrical devices and motors. It yields itself readily to magnetization.
- Unlike other types of carbon steel, which tend to be brittle, mild steel is hard as well as malleable, making it the best choice for use in construction of pipelines, building materials and many other daily-use essentials like cooking-ware.
- Mild steel can be machined and formed efficiently because of its intrinsic adaptability. It can be solidified with carburizing, making it the perfect material for delivering a scope of shopper items.
- The high measure of carbon likewise makes it defenseless against rust. Characteristically, individuals incline toward stainless over mild steel when they need a rust-free innovation. It is an essential ingredient of foundation (of buildings) and reinforcement to the structures. Other than these, it is also used in the auto manufacturing industry.

1.1.2 Chemical Composition of mild steel

Composition of mils steel varies from industry to industry. It depends on the degree of utilization. Table 1.1 shows the general composition of mild steel.

Table 1.1 General Composition of Low Carbon Steel

Element	Content
Carbon (C)	0.14 - 0.20 %
Iron (Fe)	98.81 - 99.26 % (as remainder)
Manganese (Mn)	0.60 - 0.90 %
Phosphorous (P)	≤ 0.040 %
Sulphur (S)	≤ 0.050 %

Note: Adapted from *International Journal of Advanced Trends in Computer Science and Engineering*, Vol.2, No.6, Pages: 61-63 (2013)

1.2. Corrosion

In the presence of a chemical environment or due to any chemical process, metal and alloys of metals undergo gradual destruction/deterioration. This phenomenon of decay is known as Corrosion. In simple terminology, corrosion processes involve the reaction of metals with environmental species. According to IUPAC, “An irreversible reaction of a material (e.g., metal, ceramic, and polymer) with its surrounding/environment which results in consumption of the material or its dissolution into the environment". Corrosion doesn't always mean the deterioration or decay of metal. The process of melting, mechanic fracture, abrasion or evaporation are out of the domain of corrosion. The meaning of corrosion need be further broadened to incorporate microbial impacted variables. Corrosion is the reverse of extractive metallurgy. It is the slow process of conversion of metal to its ore form or the naturally stable form (Fontana J Mars, 2013).

1.2.1. Corrosion Mechanism

If mild steel is exposed to an aerated neutral aqueous solution, for example, a dilute solution of sodium chloride in water, then the initiation of corrosion will take place on deformities/defects on the surface (Perse J, 2001). These errors may be attributed to mechanical damage such as scratches or due to natural discontinuities in the film formed on the surface, i.e. grain boundaries or composition defect of the steel.

At every deformity, the steel is presented to the electrolyte and an anodic response happens, bringing about the development of iron particles and free electrons. These electrons are then led through the oxide film to participate in a cathodic action at the surface of the film. Cathodic action requires the presence of dissolved oxygen in the electrolyte and results in the development of hydroxyl.

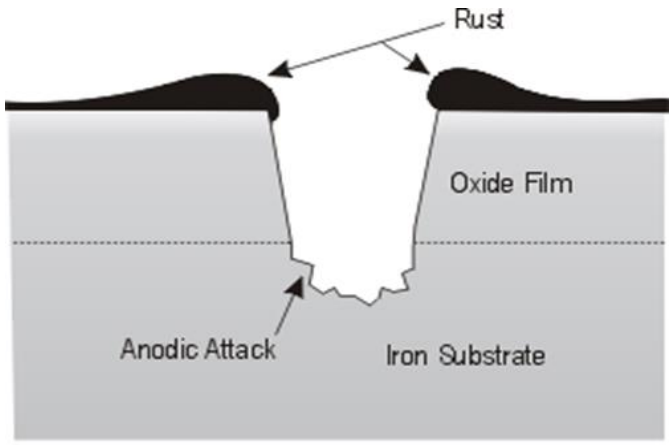


Figure 1.1 Corrosion Mechanism of Pitting type Corrosion (Azom.com, 2015)

Adapted from *http://www.azom.com/article.aspx?ArticleID=91.)*.

The hydroxyl particles react with the ferrous particles delivered by the anodic action to produce ferrous hydroxide, which is then changed over into a hydrated oxide called, rust. Step by step, a scab of rust may shape over the highest point of the pit. However, this is so permeable it couldn't

be possible to block the anodic zone entirely. Semi-permeability allows the corrosion mechanism to continue, bringing about more profound assault and broadening of the anodic range as the surface oxide film splits away.

Internal corrosion is a real reason for pipeline deteriorations and can approach 50% of all occurrences. Pipeline failure is mostly because of setting an area of limited corrosion. Real pipeline failures rates rely on upon the setting rate and the wall thickness.

Despite the fact that the crucial component of corrosion includes creation or presence of corrosion cells, there are a few sorts or types of corrosion that can happen. It ought to, in any case, be borne at the top of the priority list that for corrosion to occur, there is no requirement for discrete (physically free) anodes and cathodes. Endless micro level anodic and cathodic regions can be created at the same (single) surface on which anodic (corrosion) and cathodic (reduction) responses happen. Every type of corrosion has a particular plan of anodes and cathodes and specific examples and areas relying upon the type can exist.

1.2.2 Different Types of Corrosion

1.2.2.1. General Attack Corrosion:

It also known as uniform attack corrosion, general attack corrosion is the most common type of corrosion and it is caused by an electrochemical reaction that results in the deterioration of the entire exposed surface of the metal or alloy. Eventually, the metal decays to the point of failure. This type of corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, because it is predictable, manageable and often preventable.

1.2.2.2 Localized Corrosion:

Differing from general attack corrosion, Localized Corrosion precisely targets an area of the metal or alloy structure. Localized corrosion is classified into three types that are as following:

• **Pitting corrosion: -** It is a localized event restricted to smaller areas. Formation of micro-pits is very damaging. Local Concentration cells involving oxygen and other ion gradients can kick-start pitting through the formation of anodic and cathodic areas. Chloride ions have detrimental action to the passive films and can make pit formation auto-catalytic by supplementing the reaction. Measurement of pitting potentials can predict the pitting tendency. "Pitting Factor" (ratio of deepest pit to average penetration) can be used to evaluate the severity of pitting corrosion that is usually observed in passive metals and alloys. Similarly, critical pitting temperature is also a helpful parameter in understanding the phenomenon.

•**Crevice corrosion**: - Another type of localized corrosion similar to pitting, crevice corrosion also occurs at a precise location. It is associated with micro-ecosystem supporting corrosion, similar to those found in gaskets, washers, and clamps, etc. Acidic conditions or a depletion of oxygen leads to the formation of concentration cells in a crevice, and thus causes crevice corrosion

•**Filiform corrosion**: - It occurs under coated or plated surfaces when fluid environment breaches the coating, filiform corrosion begins at small defective sites in the layer and spreads within to cause structural damage.

1.2.2.3. Galvanic Corrosion:

Galvanic corrosion, or dissimilar metal corrosion, happens when two distinct metals are found together in a destructive electrolyte. A galvanic coupling takes place between the two metals, where one metal turns into the anode and the other the cathode. The anode, or conciliatory metal,

erodes and decays quicker than it would alone while the cathode rots more gradually than it would something else.

Three conditions must exist for galvanic corrosion to occur (Corrosionpedia, 2015):

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact, and
- The metals must be exposed to an electrolyte

1.2.2.4. Environmental Cracking:

Environmental cracking is a corrosion process, often natural, that can result due to a combination of environmental factors affecting the metal. Chemicals, temperature along with stress-related conditions can result in the following types of environmental corrosion:

- Stress Corrosion Cracking (SCC)
- Corrosion fatigue
- Hydrogen induced cracking
- Liquid metal embrittlement

1.2.2.5. Flow-Assisted Corrosion (FAC):

Flow-assisted corrosion, or flow accelerated corrosion, results when a protective layer of oxide on a metal surface is dissolved or removed by wind or water, exposing the underlying metal to corrode further and deteriorate. "Erosion-corrosion occurs when a metal is exposed to flowing corrosive environment. Weight loss is often much higher than the summation of the weight loss only due to erosion and only due to corrosion. The weight loss of material in erosion-corrosion process is a

combination of electrochemical and mechanical effect. Passivity caused by film formation is absent in this case. As soon as the film is formed it is eroded by the flowing environment, bringing the new surface of the metal in contact with the corrosive environment. Although the summarized effect of erosion and corrosion is very dangerous, the mechanism of combination is still not thoroughly understood because of its complexity (Hamdy et al., 2008). Impingement and Cavitation are two other forms of flow Assisted Corrosion.

1.2.2.6. Intergranular corrosion

Intergranular Corrosion is an electrochemical attack on the grain boundaries of metal. The main reason for intergranular corrosion is intrinsic impurities, which tend to be present in higher contents near grain boundaries. These impure or imperfect boundaries are more prone to corrosion than the bulk of the metal.

1.2.2.7. De-Alloying:

"De-alloying, or selective leaching, is the selective corrosion of a particular element in an alloy. The most common type of dealloying is dezincification of unstable brass. The result of corrosion in such cases is a deteriorated and porous copper (Bell, 2015).

1.2.2.8. Fretting corrosion:

Fretting corrosion occurs as a result of repeated wearing, weight or vibration on an uneven, rough surface. Corrosion takes place in resulting pits and grooves on the surface. Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings (Lipson Charles, 1961).

1.2.2.9. High-Temperature Corrosion:

Fuels used in gas turbines, diesel engines and other machinery, which contain vanadium or sulphates can form compounds with a low melting point during combustion. These compounds are highly corrosive to metal alloys resistant to high temperatures and corrosion, including stainless steel. High-temperature corrosion can also be caused by high-temperature oxidization, sulphidation and carbonization.

1.2.3. Corrosion in Mild Steel

Corrosion is a serious problem with pipelines, tanks, reactors, carts, etc. It affects them both internally and externally. In the present case, we are considering the effects of internal corrosion in water pipelines and quenching carts. For the safe and economically sustainable operation of water pipeline, it is necessary to understand the environment to which it is exposed. It helps in determination of most probable life and safe replacement. Pipeline failures often occur due to pitting and crevice corrosion. Pitting and Crevice Corrosion occurs when corrosive water collects in traps, and there is no amenity for chemical treatment. Corrosion can take place by different methods depending upon the environment and composition of metal, although, mechanism of corrosion more or less remains same.

Iron and steel pipes are used in water distribution systems from almost over five centuries. As per thermodynamic stability, Ferric iron (Fe (iii)) is preferred state when brought in contact with atmospheric oxygen, exposure to aqueous conditions results in corrosion of iron. Table 1.2 enlists the different types of corrosion products formed with iron. All water distribution pipelines have a build-up of iron corrosion products inside the iron pipes. Corrosion scales not only restrict the flow of water but also degrade the water quality.

Table 1.2 Corrosion Products Found in Rust Layers.

Oxides	
Hematite	α-Fe_2O_3
Maghemite	β -Fe_2O_3
Magnetite	Fe_3O_4
Ferrihydrite	$Fe_5HO_8.4H_2O$
Hydroxides	
Ferrous hydroxide Fe(OH)2	$Fe(OH)_2$
Ferric hydroxide Fe(OH)3	$Fe(OH)_3$
Goethite α-FeOOH	α-FeOOH
Akaganeite β-FeOOH	β-FeOOH
Lepidocrocite γ-FeOOH	γ-FeOOH
Feroxyhyte	δ-FeOOH
Others	
Ferrous chloride	$FeCl_2$
Ferric chloride	$FeCl_3$
Ferrous sulphate	$FeSO_4$
Ferric sulphate	$Fe_2(SO_4)_3$

Note: Adapted from Article review, *Atmospheric Corrosion of Mild Steel*, 2011

1.3. Effect of Different Water Quality Parameters

Physical and Chemical properties of media/ environment affect the rate and type of corrosion.

1.3.1. Effect of temperature and pH.

Temperature accelerates the rate of corrosion pretty much as it does most different responses. In any case, the impact of temperature on corrosion can be more confused. A high water temperature decreases the solvency of calcium carbonate in water, which advances scale development and moderates corrosion. Temperature additionally adjusts the manifestation of corrosion. Pits and tubercles have a tendency to frame in chilly water while high temp water advances uniform

corrosion. Uniform corrosion spreading over the whole surface of a pipe is far less tricky than tuberculation, so high temperatures can appear to moderate the destructive procedure. An increment in the temperature causes a reduction in the stress corrosion life (Nuflowtech.com, 2015).

"The pH of regular waters is seldom outside the genuinely narrow scope of 4.5 to 8.5. High values, at which corrosion of steel may be suppressed, and low values, at which gaseous hydrogen evolution happens, are not frequently found in regular waters."(Scheers et al., 1992). In a wide scope of about pH 5 to 9, the corrosion rate can be communicated just as far as the measure of DO present. At about pH 4.5, acidic corrosion is started, overpowering the oxygen control. At about pH 9.5 or more, deposition of insoluble ferric hydroxide has a tendency to smother the corrosion assault.

1.3.2. Effect of flow velocity

The impact of flow velocity on corrosion is additionally rather complex. Moderate flow rates are the most suitable since they advance the development of scale without loosening up tubercles. At low flow speeds, corrosion is expanded and has a tendency to be as pits and holes because of the presence of oxygen concentration cell corrosion. At high flow rates, abrasion of the water against the pipe has a tendency to wear the pipe away in an altogether different manifestation of corrosion. High flow speeds likewise evacuate inhibiting scale and tubercles and enhances the contact of the pipe internals with oxygen, all of which will expand the rate of corrosion.

1.3.3. Dissolved gas

Oxygen is a cathodic depolarizer that reacts with and removes hydrogen from the cathode during electrochemical corrosion, thereby permitting corrosion attack to continue. The effect of oxygen on corrosion with metal in a closed vessel increases with temperature.

Dissolved oxygen (DO) is an important electron acceptor in the corrosion of metallic iron. DO can also play a role in the oxidation of ferrous iron (Fe+2) or iron scales.

$$Fe\ (metal) + 0.5O_2 + H_2O \leftrightarrow Fe^{+2} + 2OH^-$$

$$Fe^{+2} + 0.25O_2 + 0.5H_2O + 2OH^- \leftrightarrow Fe\ (OH)_{3\ (s)}$$

$$3FeCO_{3\ (s)} + 0.5O_2 \leftrightarrow Fe_3O_{4\ (s)} + 3CO_2$$

$$4Fe_3O_{4\ (s)} + O_2 \leftrightarrow 6Fe_2O_{3\ (s)}$$

Thus, the oxygen concentration can have varying effects on iron corrosion. As expected, the corrosion rate increases with increasing DO. Higher turbidity is seen at lower oxygen saturation, but it is also reported that water free of DO will not tuberculate.DO is also responsible for the ability to buffer ions, including phosphates, to inhibit corrosion. (http://nuflowtech-com.web30.winsvr.net/Portals/0/pdfs/Iron_Pipe_Corrossion.pdf)

1.3.4. Effect of Sulphur and its compounds.

Mild steel is a well-known structured material in the petroleum industry due to its low cost, good mechanical and corrosion resistant properties. Most common type of Sulphur compounds are sulphates, sulphites and sulfides. The presence of sulphide, in the fluid can affect the performance of mild steel in the petrochemical industry, as this phenomenon is responsible for costly economic and human loss. (Hamdy et al, 2008). Sulphide pollution of seawater can occur from the industrial waste discharge, biological and bacteriological process in seawater, which enhances the corrosion

of steels. The solution speed in the presence of suspended particles such as sand or fine waste particles and aggressive ions such as chloride and sulphide can have a marked effect on the corrosion inhibition performance of mild steel.

Both iron and Sulphur species are susceptible to oxidation and Sulphur produces oxides quickly to sulphates and sulphites that can increase the acidity of the flowing fluid. Elemental Sulphur can readily form in aqueous systems via the oxidation of sulphide species. Possible reactions for the formation of elemental Sulphur (S_8) could involve high oxidation state metal (In equation denoted by Mn+) or oxygen:

$$8\ H_2S_{(aq)} + 16\ Mn^{+}_{(aq)} \rightarrow S_{8\ (s)} + 16\ H^{+}_{(aq)} + 16\ M\ (n-1)^{+}_{(aq)} \quad (1)$$

$$8H_2S_{(aq)} + 4O_{2\ (g)} \rightarrow S_{8(s)} + 8H_2O_{(l)} \quad (2)$$

In addition to chemical processes, sulphide oxidizing bacteria have been shown to form liquid Sulphur droplets under ambient conditions; consequently, the formation of elemental Sulphur is almost inevitable in H_2S corrosion environments in the field. Elemental Sulphur is shown as S_8 in the reaction equations below as that represents the stable allotrope of Sulphur under standard conditions Acidification in Sulphur containing aqueous systems has been reported, with species such as H_2S, H_2SO_2, H_2SO_3, H_2SO_4 and polysulfide being possible candidates as hydrolysis products. Acid formation as a result of Sulphur hydrolysis was the primary factor governing corrosion in the presence of elemental Sulphur (Fang H et al, 2008).

$$S_{8\ (s)} + 8\ H_2O\ (l) \rightarrow 6\ H_2S_{(aq)} + 2\ H_2SO_{4\ (aq)}$$

Alternatively, (MacDonald et al, 1978) hypothesized, "An electrochemical reaction between iron and polysulfide is the driving force for corrosion in systems where elemental Sulphur is present."

1.3.5. Chlorine Compounds

Chlorine is a very strong oxidizing agent for all metallic and organic species present. The reaction with iron:

$$HOCI + 2Fe^{++}\ 5H_2O \rightarrow 2Fe\ (OH)_3\downarrow + Cl^- + 5H$$

Corrosion behavior was studied of different materials in field environments and reporting weight loss, corrosion rate, and localized corrosion. Chlorine is available as liquid chlorine in steel compartments, as NaOCl solution, as calcium hypochlorite granules, and at times as chlorine dioxide ($C1O_2$).

The essential resistance of stainless steel happens in light of its capacity to shape an inhibiting layer on the metal surface. This covering is a passive film that opposes further oxidation or rusting. The formation of this film is instantaneous in an oxidizing air, for example, air, water, or different fluids that contain oxygen. When the layer has framed, we say that the metal has become passivized, and the oxidation or rusting rate will ease off to under 0.002 every year. Chlorides quickly penetrate this passive film and will allow the corrosive attack to occur.

The accelerated form of chemical attack is greater in some areas than others. It occurs when the corrosive environment penetrates the passivized film in only a few areas as opposed to the overall surface. As stated earlier, chlorides will penetrate passivated steel. Pit type corrosion is, therefore, simple galvanic corrosion, occurring as the small active area is being attacked by the large passivated area. This difference in relative regions quickens the corrosion, creating the pits to enter deeper. The electrolyte fills the pits and keeps the oxygen from passivating the active metal, so the issue deteriorates. This sort of corrosion is frequently called concentrated cell corrosion.

In the event that the metal piece is under tensile stress, either due to the operation or lingering stress left between productions, the pits formed in a past run will extend. Since the piece is under

tensile stress, cracking will happen in the stressed area. Ordinarily, there will be more than one split present bringing about the sample to look like a cobweb's. Chloride stress cracking is a difficult issue in the industry and not frequently perceived by the individuals. Some extra information about chloride stress breaking that we need to know:

• Chlorides are the big problem when using the 300 series grades of stainless steel. The 300 series is the one most commonly used in the process industry because of its good corrosion resistant proprieties.

• Beware of insulating, or painting stainless steel pipe. Most insulation contains chlorides and piping is frequently under tensile stress. The worst condition would be insulated, steam traced, stainless steel piping.

1.3.6. Bromine Compounds

If you pass bromine vapor over a hot iron, a similar, but slightly less vigorous reaction happens, this time producing iron (III) bromide. Anhydrous iron (III) bromide is usually produced as a reddish-brown solid. Again the iron has been oxidized to an oxidation state of +3.

1.3.7. Iodine Compounds

The reaction between hot iron and iodine vapor only produces iron (II) iodide, and is much less Vigorous. The iron (II) iodide is grey in appearance. Iodine is only capable of oxidizing the iron as far as the +2 oxidation state.

1.3.8. Cyanides

Cyanide is a triple-bonded molecule with a single negative charge consisting of one atom of carbon in the +2 oxidation state and one atom of nitrogen in the -3 oxidation state". An immensity of

cyanide amount in the environment is mainly due to metal finishing and mining industries. Different forms of cyanide include free cyanide, cyanide ion, cyanide salt, metallic cyanide complexes and synthetic organic cyanides, also known as nitriles and total cyanide. Cyanide occurs in water as hydrocyanic acid (HCN), cyanide ion (CN-), simple cyanides, and metallic cyanide complexes and as simple chain and complex ring compound.

The behavior of mild steel in aqueous cyanide solutions similar to caustic cyanide elution solutions was investigated at high temperature in electrochemical experiments. The anodic polarization diagrams of mild steel indicated that steel may undergo active dissolution under these conditions. The presence of cyanide will favor the dissolution of iron to form a ferrous cyanide complex Cyanide in aqueous solution may change the behavior of iron by the formation of soluble iron cyanide complexes in preference to insoluble oxides.

At higher concentrations of either hydroxide or cyanide gave rise to an increase in the active peak current densities. Cyanide additions caused the active potential region to expand and increased the peak current densities significantly. This effect was more pronounced at higher hydroxide concentrations, but increased current densities were also noted at lower pH values. At pH less than 11 cyanide ions combines with hydrogen. At pH greater than 12, CN- ions are available in the free form. In the presence of other general effluent components like ammonia, hydrogen sulphide and carbon dioxide, cyanide ions causes increased corrosion rates in carbon steels. Cyanide concentrations in the range of 20 to 100 ppm are present in industrial wastes. Corrosion rate increases with increase in temperature and cyanide content.

1.4. Corrosion inhibition

Erosion and scaling of carbon steel may be restrained by the utilization of inhibitors. It has been watched that the impact of corrosion inhibitors is constantly brought about by a change in the condition of the protected surface because of deposition or development of barely soluble compound with metal cations. A survey including broad listing of different sorts of natural inhibitors has been published. The frequently utilized corrosion inhibitors are nitrogen, Sulphur, oxygen and phosphorous containing mixes. These mixes get adsorbed on the metal from the bulk of the environment and construct a film on the metal surface. The inhibition efficiency (IE) increments in the request O<N<S<P.The erosion inhibition of metals in acidic media by different of natural mixes has been broadly studied. The inhibition activity of natural atoms is because of their adsorption on the surface of the metal through the presence of activity centers.

1.5 Scope of Project

Literature review suggests that a vast amount of work has been done in this field. Although it is an interesting topic from last two centuries, most of the notable work is confined to a particular environment. There has been very little work constituting multiple corrosive agents. It is known fact that Industrial effluents are the major cause of corrosion. Industrial effluents contain more than one component in it with concentration continuously varying due to large scale operations. To develop a corrosion inhibition mechanism for an industry, it is must that we understand the corrosion at that large scale. The understanding can be used to develop an inhibition technology and corrosion predictive modelling. Predictive modelling can help in determination of life span of a machinery used in corrosive environment. So far researchers have studied a large number of corrosive environment but no any significant work has been done to collect and standardize these data.

1.6 Objective

As discussed in last section, most of the corrosion studies have been done for individual component effluent. Mild steel is the most used metal and accounts for maximum loss due to corrosion. An economical method developed to inhibit corrosion in mild steel can drastically reduce the amount of money, governments all around the world are losing. The objective of current research is to understand the corrosion due to quenching effluent of Rourkela steel Plant. As the effluent concentration are more or less same in similar industry, the understanding of corrosion from wastewater can be used in other quenching units and steel plants.

The major objectives of the current investigation are as following:

- Determination of corrosion behavior and type using Surface Morphology Techniques.
- Determination of the corrosion rates under the influence of various concentration of individual chemicals and combination of chemicals.
- Determination of corrosion Inhibition efficiency of an inhibitor.

CHAPTER 2

Materials and Methods

2.1 Chemicals and Reagents

All the chemical reagents like Silver Nitrates, other sulphates, chlorides and cyanides were of analytical grade. All the chemicals were procured from Merck, Fischer and HIMEDIA.

2.2 Mild Steel Coupon

Mild steel coupon with the dimension of 2.35cm X 0.95cm X 0.1cm was used as test sample to study the effect of corrosion by weight loss. Sample was obtained as bulk metal from Rourkela Steel Plant, SAIL and cut into the desired dimension using diamond wires. Sample was cleaned with emery paper of grades 80, 100 and 200 respectively to ensure a smooth filmless surface. To verify the legitimacy of the data produced, a few experiments were done twice and thrice to assure reproducibility.

2.3 Scanning electron Microscopy

Metal Coupon were cleaned with emery paper of multiple grits in the range of 80-300. The coupon obtained was washed and cleaned. The Scanning Electron Microscopy was done using JEOL Scanning Electron Microscope. The resolution and magnification range of SEM was 3.5 nm and '10X to 400,000 X' respectively. Corroded samples for SEM imaging was obtained from Rourkela Steel Plant. Ii was a part of machinery equipment replaced due to corrosion.

2.4 Wastewater collection and Preservation

Wastewater was collected from quenching pit of Rourkela Steel Plant. Water sample was collected in a plastic bottle and stored at temperature below 4˚C. Wastewater was divided into three parts

and preserved with different reagents as per the demand of the experiments to be performed. Samples were stored at pH <2, Temp-4˚C (Using HNO_3 or H_2SO_4), pH>10, Temp- 4˚C (Using NaOH). EPA guidelines were used for determination of composition of wastewater.

2.5 Preparation of Stock Solution

Stock solution of Sulphates, Chlorides and Cyanides and Nitrites were prepared by dissolving compound having 1 gram of the ions concerned in 1000ml of water. It produced the stock solution. The solution was further diluted as per the concentration required. Sodium Chloride, Ammonium Sulphate, Potassium Ferricyanide and Potassium Nitrite are the compounds used for the preparation of stock solutions.

2.6 Weight Loss by Corrosion at Room temperature.

Electrolyte/ Corrosive environment of varying concentrations were prepared and kept in a bottle/container of 300ml capacity. After recording of initial weights, Metal coupons were dipped into the corrosive media using a thread attached to the cork covering the bottle opening. The samples were left in this state unscathed and undisturbed for a period of seven days. It was done to allow proper time for corrosion to take place. After the completion of seven day period metal coupons were taken out and cleaned with jet of water and lightly scrubbed to remove loosely bounded scales. Sample was weighed to measure the direct corrosion loss. Sometimes Increase in weight was reported showing deposition of scales.

Scale and film formed on Surface was cleaned using metal brush and sample was weighed to determine overall corrosion rate and weight of scales.

2.7 Weight Loss by Corrosion at 100˚C

Two mild steel coupons were exposed to boiling corrosive environment at 100˚C. Corrosive media was boiled in a flask by heating mantle. A condenser setup was used to ensure that the concentration of the electrolyte remains unchanged. Samples were exposed for half an hour in one single run. Multiple runs were done in a few cases to verify the reproducibility of data. Once the experiment was complete, samples were immediately removed from the corrosive media to avoid error due to prolonged exposure. Samples were cleaned by jet of water and soft scrubbing to remove any loosely bounded scales. Sample was weighed to determine direct corrosion loss.

Scale and film formed on Surface was cleaned using metal brush and sample was weighed to determine overall corrosion rate and weight of scales.

CHAPTER 3

Results and Discussions

In the present study we determine the properties of material and environments, the two factors playing a major part in corrosion. Properties of the environment i.e. pH, turbidity, dissolved oxygen content, biological and chemical oxygen demand, concentration of various chemical components present. Sample was collected from Coke Quenching pit of SAIL, Rourkela. Different set of methods and preservation techniques were used to preserve the composition of the sample till the time of analysis. For metal sample weight loss in corrosive environment was used to determine their susceptibility to the environment. Weight loss were measured in two different temperature. One low temperature at ambient and other at 100˚C.

3.1 Environment Analysis.

Industrial Waste Water sample from Rourkela Steel Plant, which acts as an environment for their quenching, waste water treatment and pumping unit was used to determine the nature of the corrosive environment. On analyzing the sample for different components, using various methods suited to them, composition of the industrial water is enlisted in Table 3.1.

Table 3.1 Analysis of waste water from Coke quenching Plant

Component	Amount in ppm	
	Run 1	Run 2
Phenol	70.08	72.81
Sulphate	7.68	18.2
Chloride	223	192
Nitrite	0.2	0.34
Ammonia	116.8	
Total Kjeldahl Nitrogen	246.6	

3.2 SEM & EDX Analysis

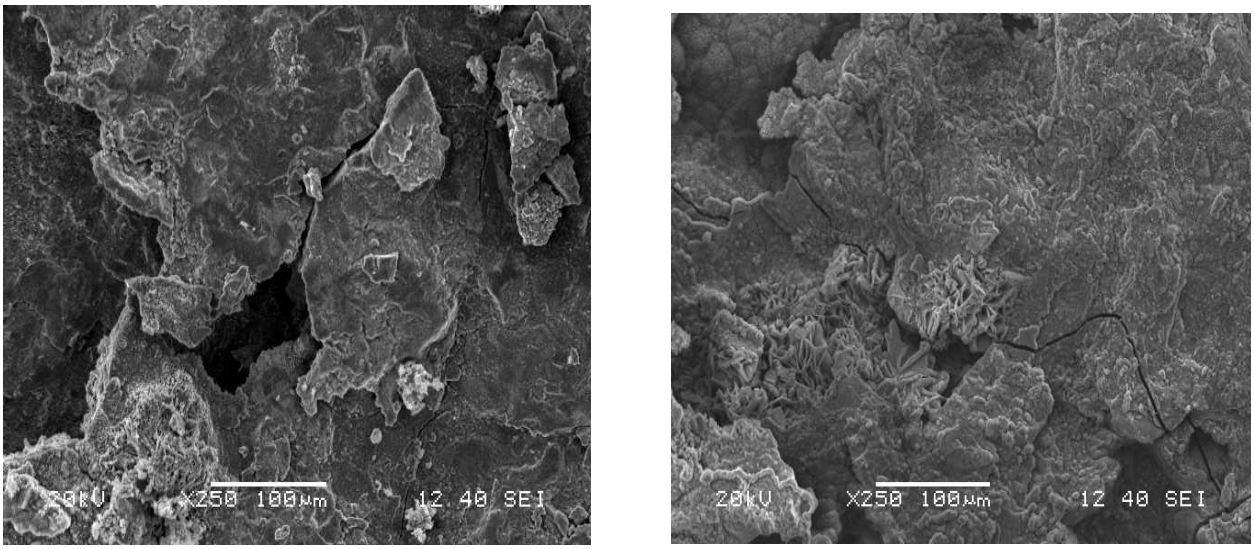
Scanning Electron Microscope was used to understand the nature of deterioration of the test sample. Figure 3.1 shows the image taken from SEM. Localized corrosion e.g. Pitting, Cracking can be seen. EDX analysis was done to determine the composition of fresh sample as well as a corroded sample. It was studied to contrast the change brought in composition of surface due to corrosion. Table 3.2 and Table 3.3 enlists the data recorded by EDX for Corrosion free and corroded sample respectively.

Table 3.2 Composition of Corrosion free steel sample

Components	Weight %
Iron	95.35
Carbon	2.53
Nickel	0.49
Cadmium	0.04
Zinc	1.24
Titanium	0.10
Lead	0.25

Table 3.3 Composition of corroded steel.

Component	Weight (%)
Iron	60.88
Carbon	6.62
Oxygen	28.77
Magnesium	0.93
Aluminium	0.25
Silicon	0.04
Sulphur	1.44
Cadmium	1.09



(a) **(b)**

Figure 3.1 Surface deterioration by (a) Pitting and (b) Cracking.

3.3 Weigh Loss Experiment

Weight Loss experiments are a popular way to determine the corrosion rate. Metal is kept in a corrosive environment for a definite period of time. Reduction in mass is measured and is generally represented in terms of cm/yr.

3.3.1 Corrosion of Sample at Room Temperature.

Sample was tested under various concentration of multiple electrolytes to determine the critical concentration at which the corrosion rate is maximum. Sample was kept in the corrosive environment for a period of seven days. A long duration of contact was necessary to understand the real effect of industrial corrosions. Electrolyte value for each concentration was 200ml. Initial weight and mass of corroded sample with and without scales gives direct loss and overall loss due to corrosion.

3.3.1.1 Effect of Chloride

Corrosion rate for chlorides were evaluated in the concentration range of 0-250 ppm. NaCl was used as a source of chloride. Corrosion rate was been found to increase initially in the concentration range of 10-50 ppm (Fig 3.2) but decrease as the concentration is increased. This decrease in corrosion rate is due to the formation of strong passive film over the surface which prevents metal from further corrosion. Corrosion rate is almost stagnant in the region of 100-200 ppm due to this passivity. Figure 3.2 shows the variation of corrosion rate with concentration of chloride ions. A small fluctuation is observed in low concentration range of 10-20 ppm. Chloride is highly responsible for localized corrosion. Due to its small size it readily replenishes the ion concentration of pits.

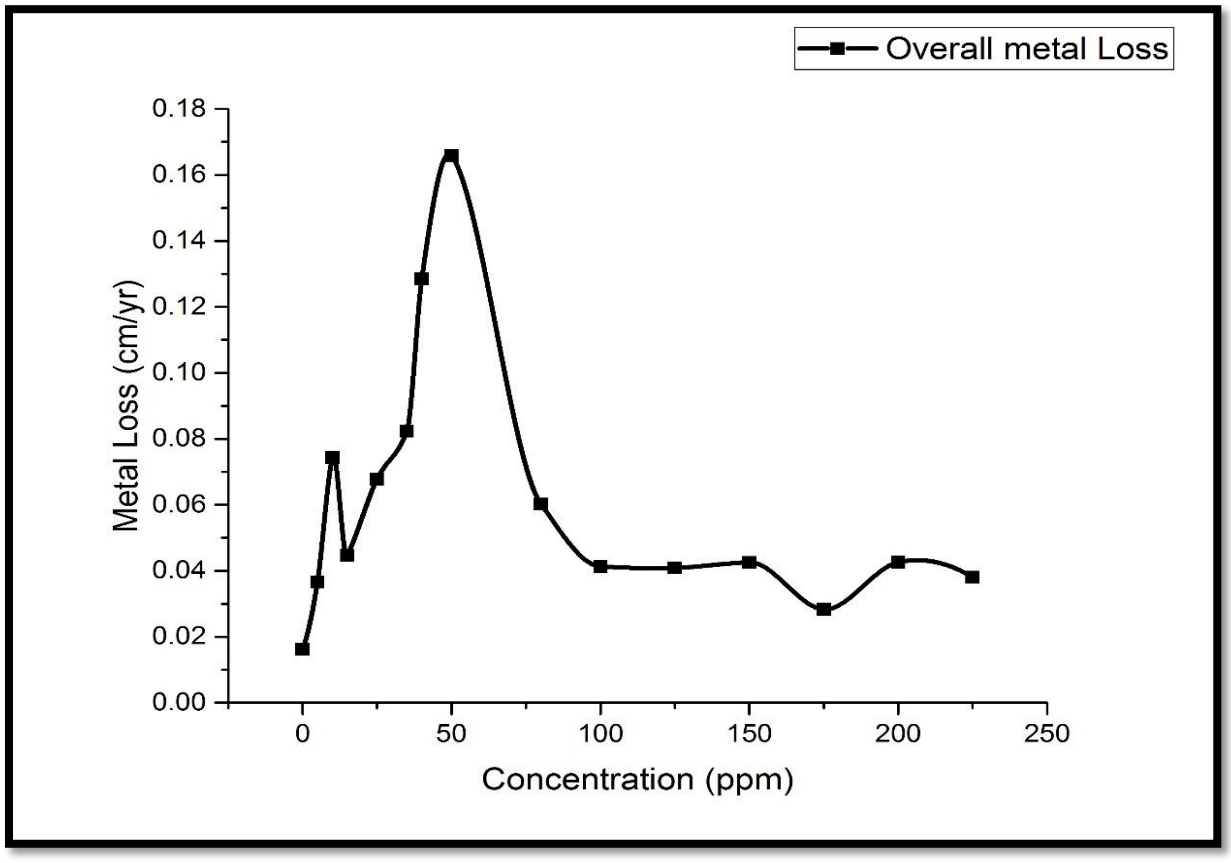


Figure 3.1 Variation in corrosion rate with concentration of chloride ions.

3.3.1.2 Effect of Sulphates.

Direct metal loss rate has been almost consistent over the concentration range of 5-20ppm. Figure 3.3 shows the variation in corrosion rate with concentration of sulphate ions. Direct metal loss has shown an increasing tendency beyond 20ppm concentration. Variation of overall metal loss to direct loss tends to confirm the effect of passivity due to film formation. Whenever overall metal is increasing, a downward shift can be observed in direct metal loss.

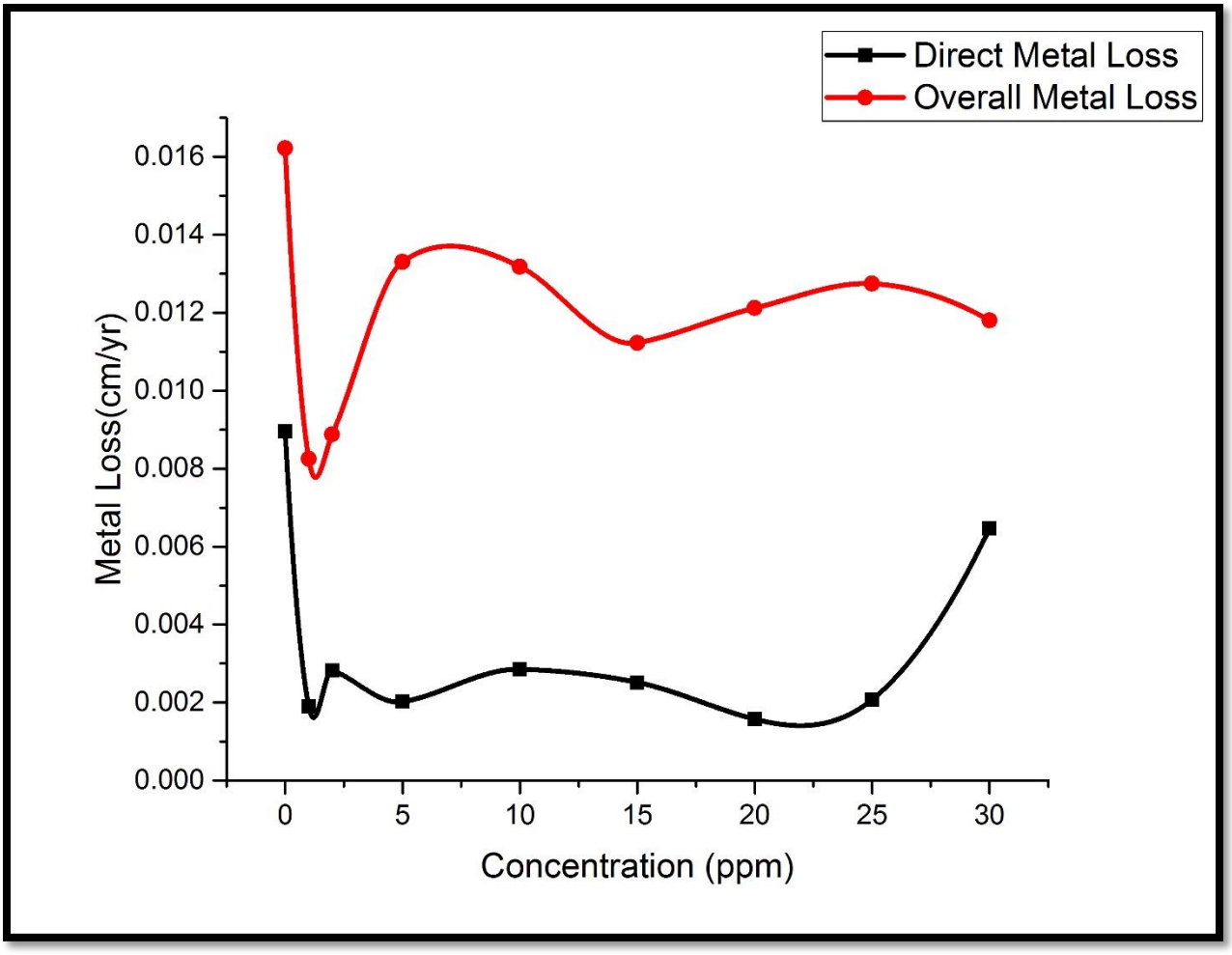


Figure 3.2 Variation in corrosion rate with concentration of Sulphate ions.

3.3.1.3 Effect of Cyanides.

Ferricyanides are highly corrosive in nature. Corrosion rates have a positive trend with increase in concentration. Scale deposition decreases in concentration range of 20-30 ppm only to gain the momentum later. Figure 3.4 shows the variation of corrosion rate with varying ferricyanide concentration. Although the direct loss and overall loss is increasing with concentration but film formed is showing a moderate resistance against corrosion. In concentration range of 30-40 ppm, slope of overall corrosion is more positive in compared to the slope of direct corrosion loss.

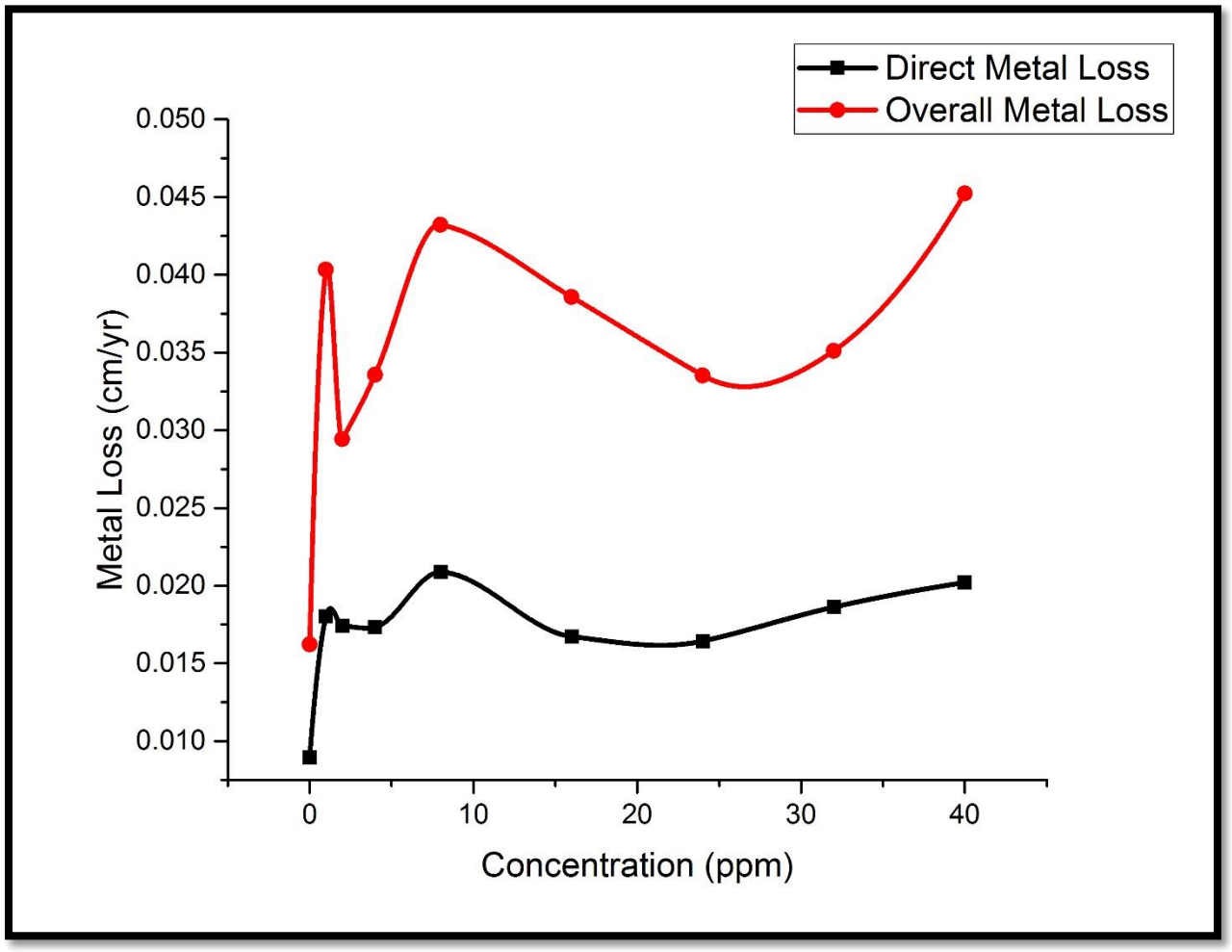


Figure 3.3 Variation in corrosion rate with concentration of ferricyanide ions.

3.3.2 Corrosion at High temperature.

Sample was boiled for a period of half an hour and weight loss was measured to understand the effect of concentration along with temperature. Corrosion rates were found to be considerably higher than the corrosion rates at room temperature.

3.3.2.1 Effect of Chloride.

Very high corrosion rates are observed with an incremental tendency with concentration. Figure 3.5 shows the variation of corrosion rate with concentration at 100˚C. General behavior of the plot is increment in corrosion rate with concentration.

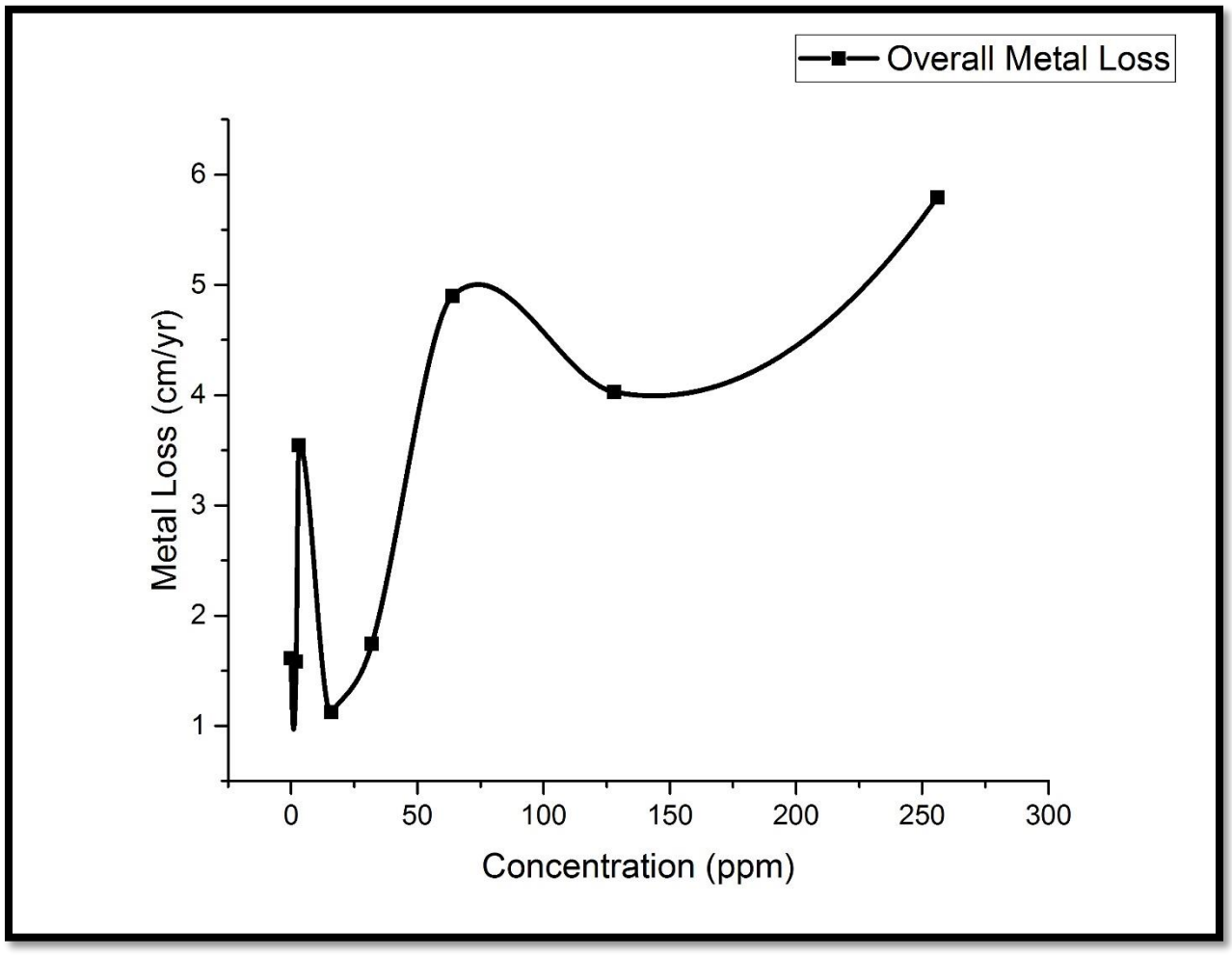


Figure 3.4 Variation in corrosion rate with concentration of chloride ions at 100˚C.

3.3.2.2 Effect of Sulphates.

Direct Metal loss is maximum at 15 ppm while overall metal loss is maximum at a lower concentration of 5ppm. The increase in direct loss is a result of weak film formation which allows the metal surface for prolonged contact with electrolyte. As concentration increases, direct corrosion tends to increase while overall metal loss decreases due to lack of film formation. Figure 3.6 shows the variation of corrosion rate with concentration of Sulphate ions.

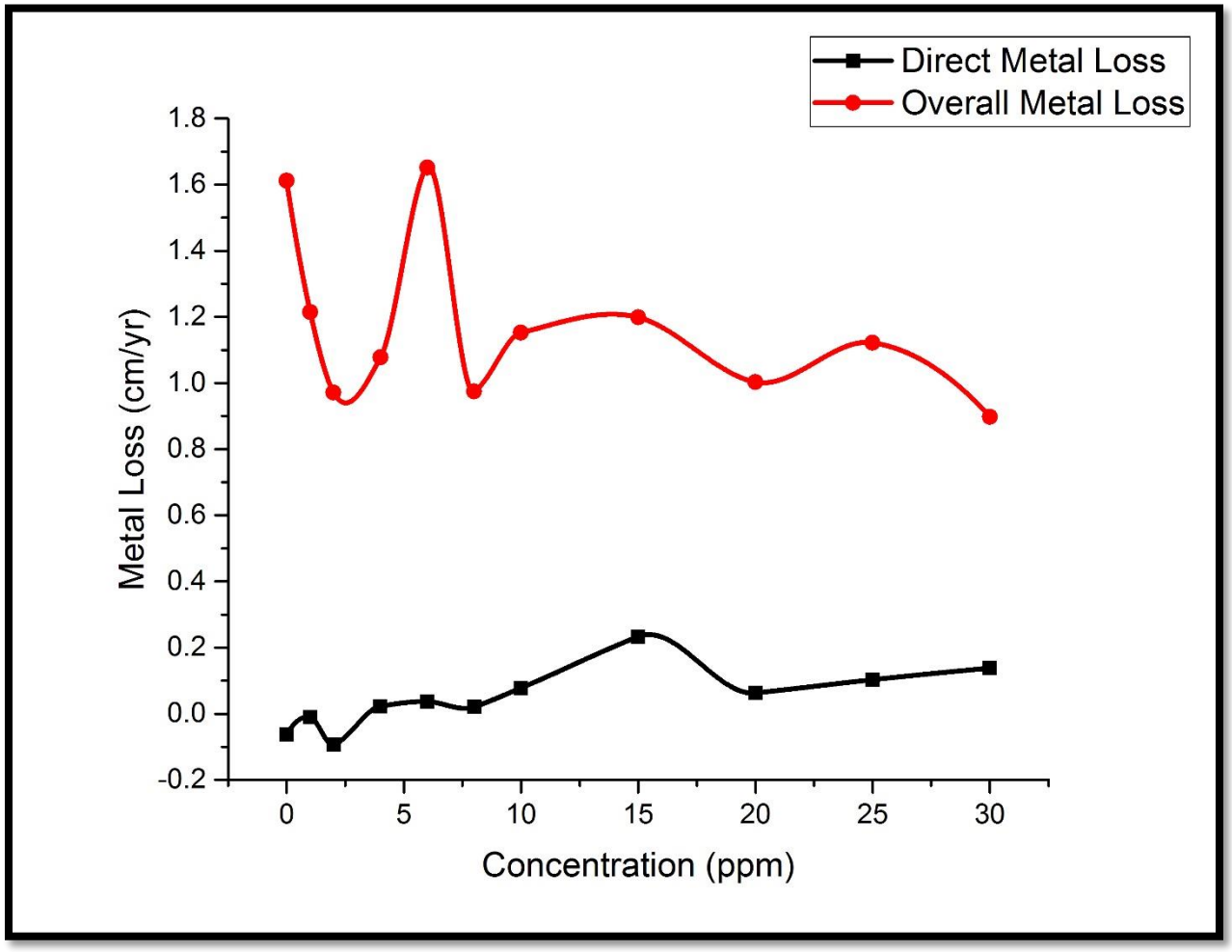


Figure 3.5 Variation in corrosion rate with concentration of Sulphate ions at 100˚C.

3.3.2.3 Effect of Ferricyanides

With increase in concentration, direct metal loss is increases almost linearly. Figure 3.6 shows the variation in corrosion rate with concentration at 100 ˚C. In low concentration range overall corrosion is high depicting large scale formation, although, in concentration range of 20-40, overall corrosion is decreasing and direct corrosion is increasing. It shows the gradual decrement in film formation as concentration increases.

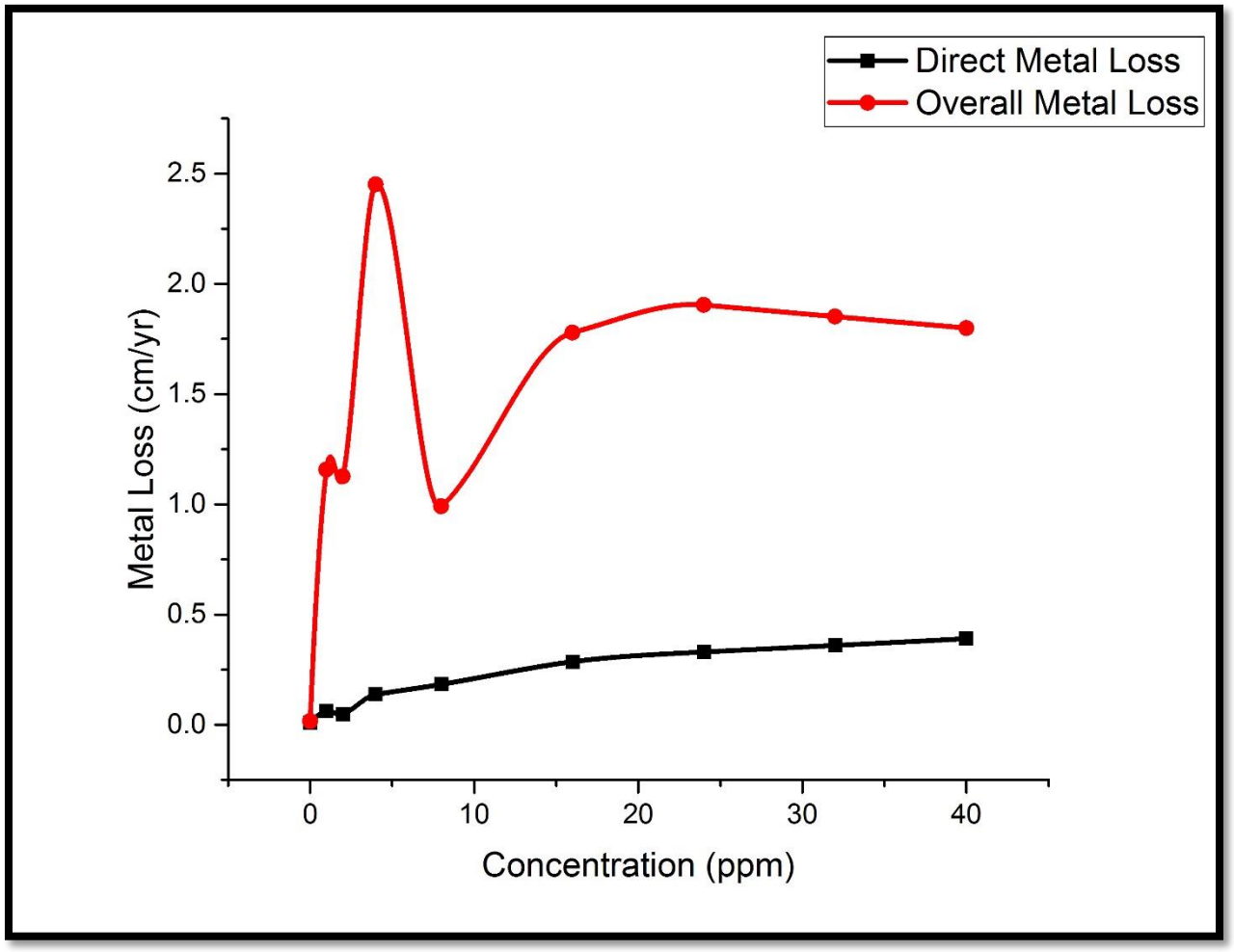


Figure 3.6 Variation in corrosion rate of test sample with varying concentration of ferricyanide ions at 100˚C.

3.3.2.4 Effect of 1:1 Chloride and Nitrite combination.

Figure 3.7 shows the variation in corrosion rates with concentration of chloride and nitrite combination at 100 ˚C .This clearly denotes the variation in direct corrosion with weight of scales formed. As overall corrosion increases, direct corrosion tends to decrease due to passive film formation. Further an interesting result is the reduced rate of corrosion when compared individually with nitrite or chloride. This shows inhibition effect one on another.

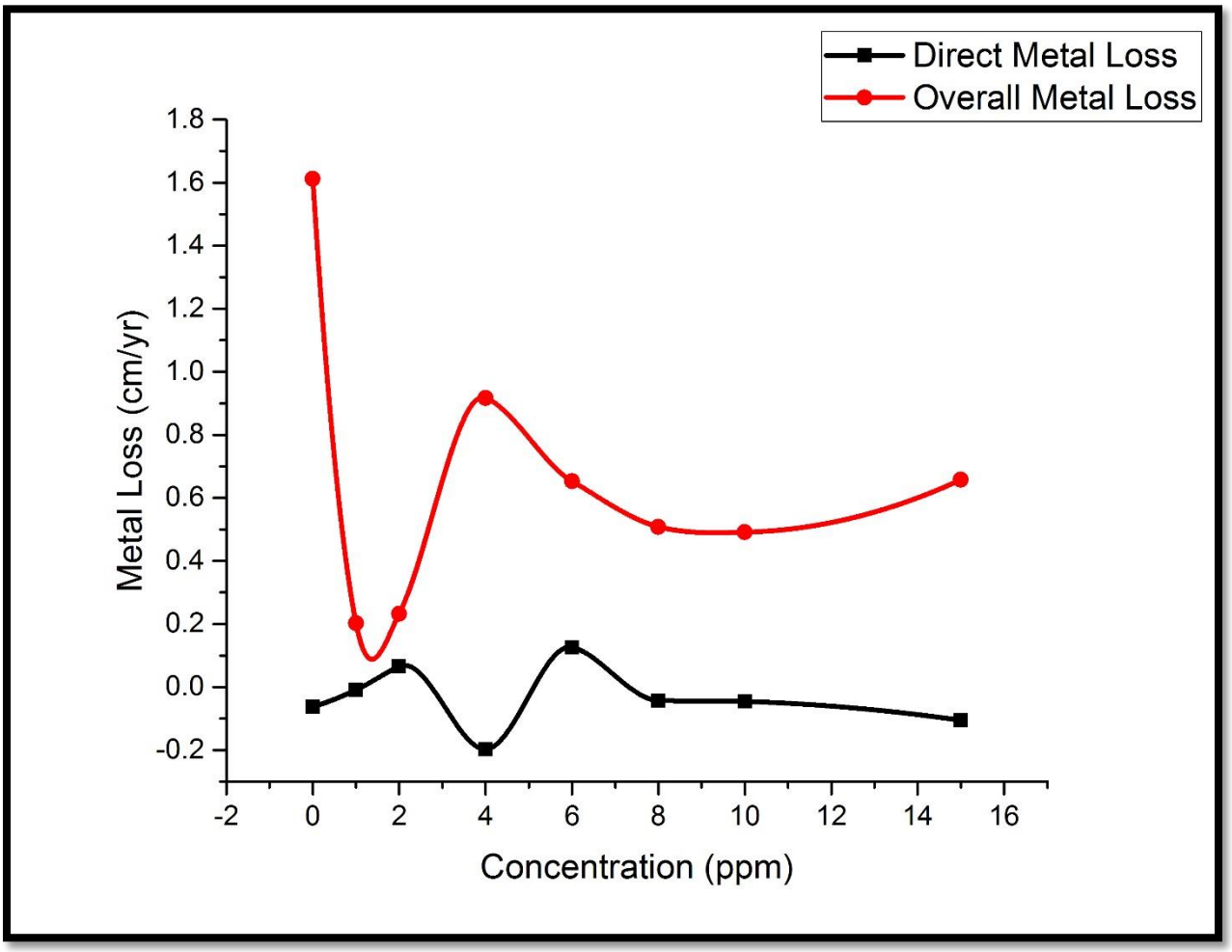


Figure 3.7 Variation in corrosion rate with concentration of 1:1 combination of chloride and Nitrite ions at 100˚C.

At 4 ppm concentration minima of direct corrosion is observed, interestingly this point corresponds to the maxima of overall corrosion.

3.3.2.5 Effect of 1:1 Sulphate and Nitrite Combination.

Combination is less corrosive than the individual electrolytes. A passive film formation is taking place. Passivity is increasing with increment in thickness of scales over surface. Figure 3.8 shows the variation of corrosion rate with concentration

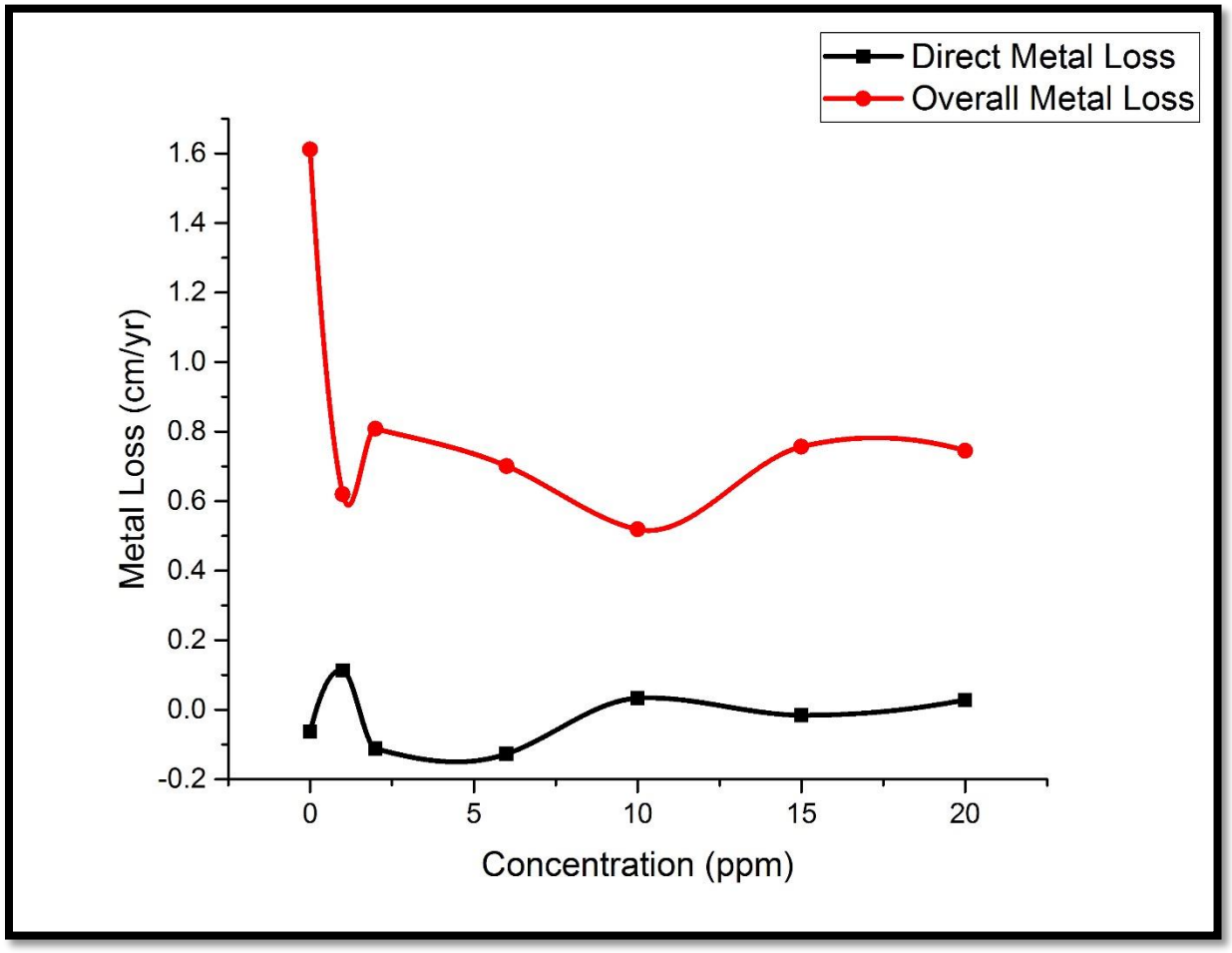


Figure 3.8 Variation in corrosion with concentration of 1:1 combination of Sulphate and Nitrite ions at 100˚C

. Direct corrosion is increasing with increasing in concentration. Maximum corrosion is taking place at 10ppm. At this point the amount of film deposition is minimum. As concentration increases in the range of 15ppm-20ppm a slight decrease in direct corrosion and an increase in overall corrosion can be seen due to increase in amount of insoluble scale deposition.

3.3.2.6 Effect of 1:1:1 combination of Sulphate, Nitrite and Chloride.

Corrosion rate are less compared to all the three individually. Although as the concentration increases, direct metal loss is decreasing with increment in overall loss. Figure 3.9 shows the variation of corrosion rate with increase in concentration of combination. With increase in concentration, weight of scale formed increases.

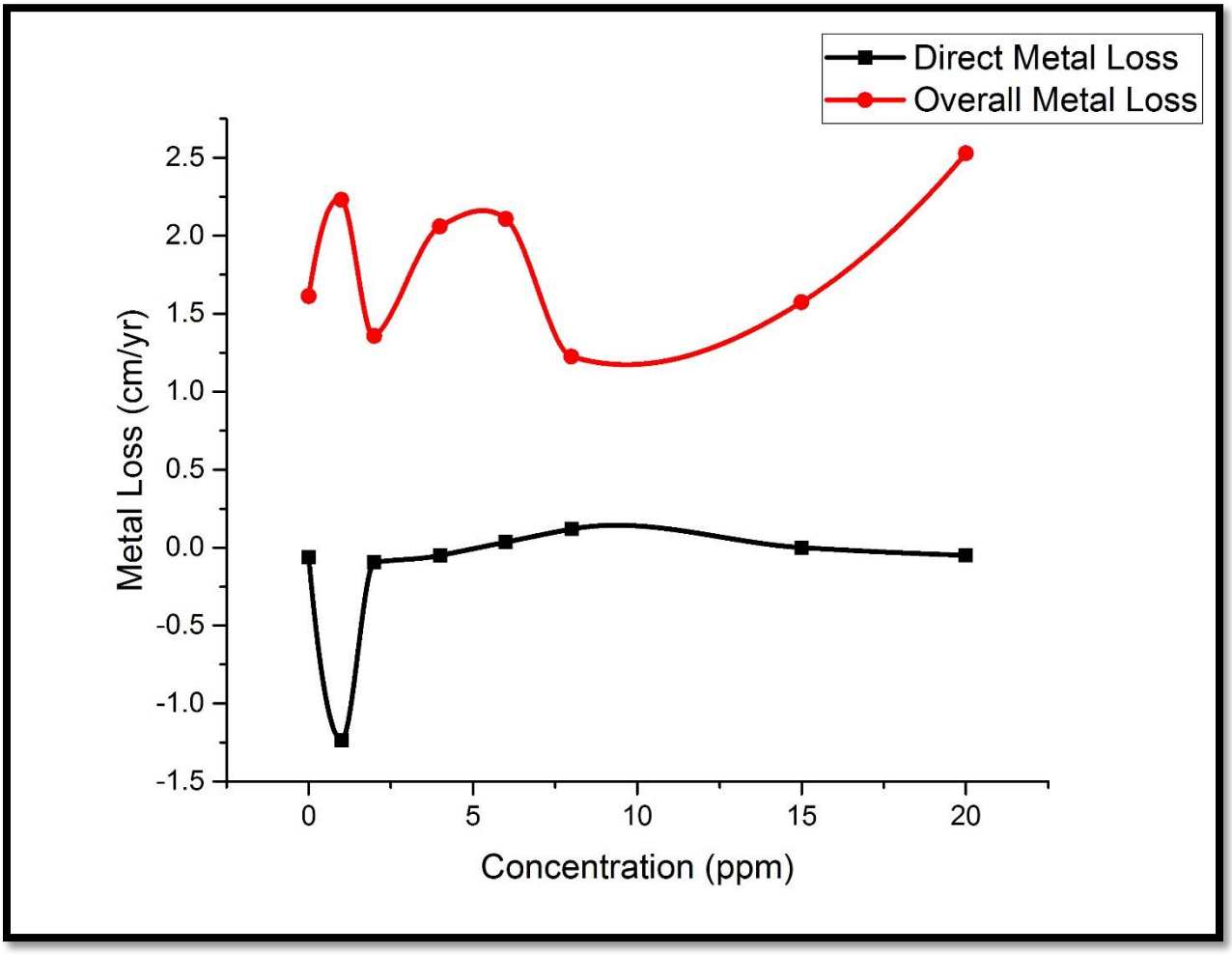


Figure 3.9 Variation in corrosion rate with concentration of 1:1:1 combination of Sulphate, Nitrite and Chloride Ions at 100˚C

3.4 Effect of Aniline as Corrosion Inhibitor.

In this part of the experiment, metal sample is again allowed to react with electrolytes. This time electrolytes have the concentration at which maximum rate of corrosion was recorded in previous experiments. Table 3.4 enlists the concentration of Chloride, Sulphate and Cyanide at which maximum corrosion was observed.

Table 3.4 Maximum corrosive concentrations.

Electrolyte	Most Corrosive conc. at room temperature.(ppm)	Most corrosive conc. At 100˚C.(ppm)
Chloride	50	250
Sulphate	5	6
Cyanide	40	40

3.4.1. Corrosion Inhibition with aniline at Room Temperature

Aniline has established itself as good corrosion inhibitor in nonferrous metals. Research has attributed its inhibiting efficiency due to fast film formation tendency. Owning to its unsaturation due to cyclic structure, they from a strong film over the electron donor metal surface. This film protects the metal from further corrosion.

3.4.1.1 Inhibition efficiency at maximum corrosive concentrations.

It is evident from the weight loss experiment at room temperature that, in presence of Aniline there is a considerable decrease in corrosion rate. Amount of scale formed has reduced as well as the corrosion (Figure 3.10). Aniline leads to a thin and strong film formation over the metal which inhibits further corrosion. Aniline has shown maximum inhibition efficiency in case of chlorides while minimum in case of Sulphates (Table 3.5). Aniline has proved itself as a great inhibitor. It forms a thin insoluble film over the metal surface.

Table 3.5 Corrosion Inhibition efficiency of Aniline at Room Temperature.

Component	Inhibition Efficiency % in Direct Loss.	Inhibition Efficiency % in overall loss.
Chloride	89.10	88.21
Ferricyanide	54.05	56.31
Sulphate	50.35	45.54

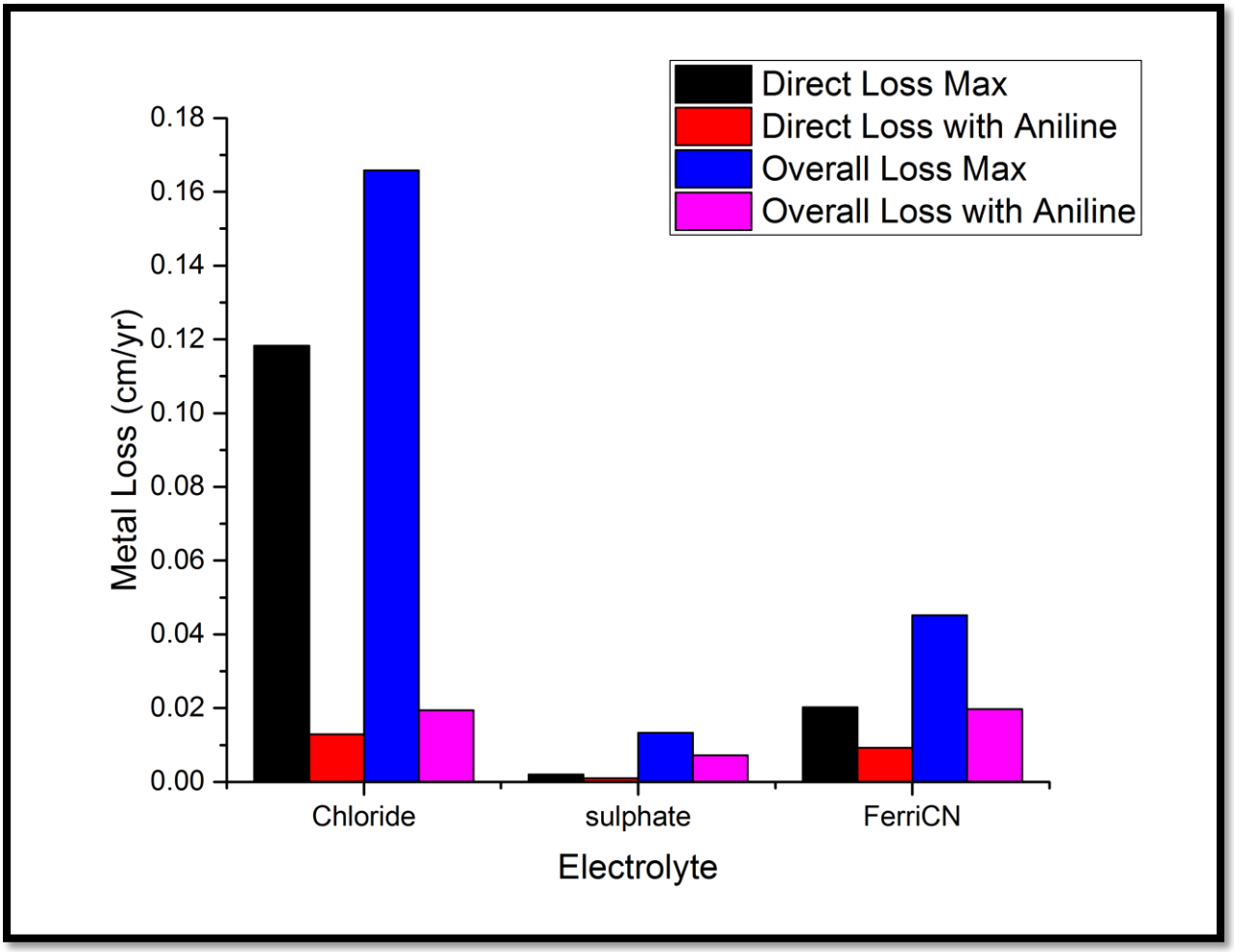


Figure 3.10 Variation of corrosion rates in presence of Aniline as an additive (1 ppm) to the solution at room temperature.

3.4.1.2 Comparison of corrosion by industrial wastewater with and without aniline.

It was found that wastewater with aniline had less corrosive tendency than the wastewater without aniline. Table 3.1 enlists the various components and their concentrations present in the waste water. Corrosion due to wastewater is combined result of all the chemical components present in them.

Table 3.6 Corrosion rates for Quenching Pit Wastewater.

Solution	Corrosion Rate for Direct Loss in cm/yr.	Corrosion rate for overall Loss in cm/yr.
Wastewater from Quenching Pit	0.00362	0.010356
Wastewater from Quenching Pit with Aniline added	0.002516	0.009782

3.4.2 Aniline as corrosion inhibitor at high temperature.

It is observed Aniline loses its knack as an inhibitor at high temperatures. Figure 3.11 shows the comparative analysis of corrosion rates at maximum corrosive concentrations, with and without aniline. Interesting observation is that in case of Phenol and Sulphate at boiling temperature, it enhances their corrosive tendency. Table 3.7 shows the inhibition efficiency of aniline at 100˚C.

Table 3.7 Inhibition efficiency of Aniline at 100˚C

Corrosive Environment	Inhibition Efficiency% in Direct Loss	Inhibition Efficiency% in Overall Metal Loss
Chloride	80.93	81.48
Ferricyanide	47.44	4.50
Sulphate	-209.10	-47.06

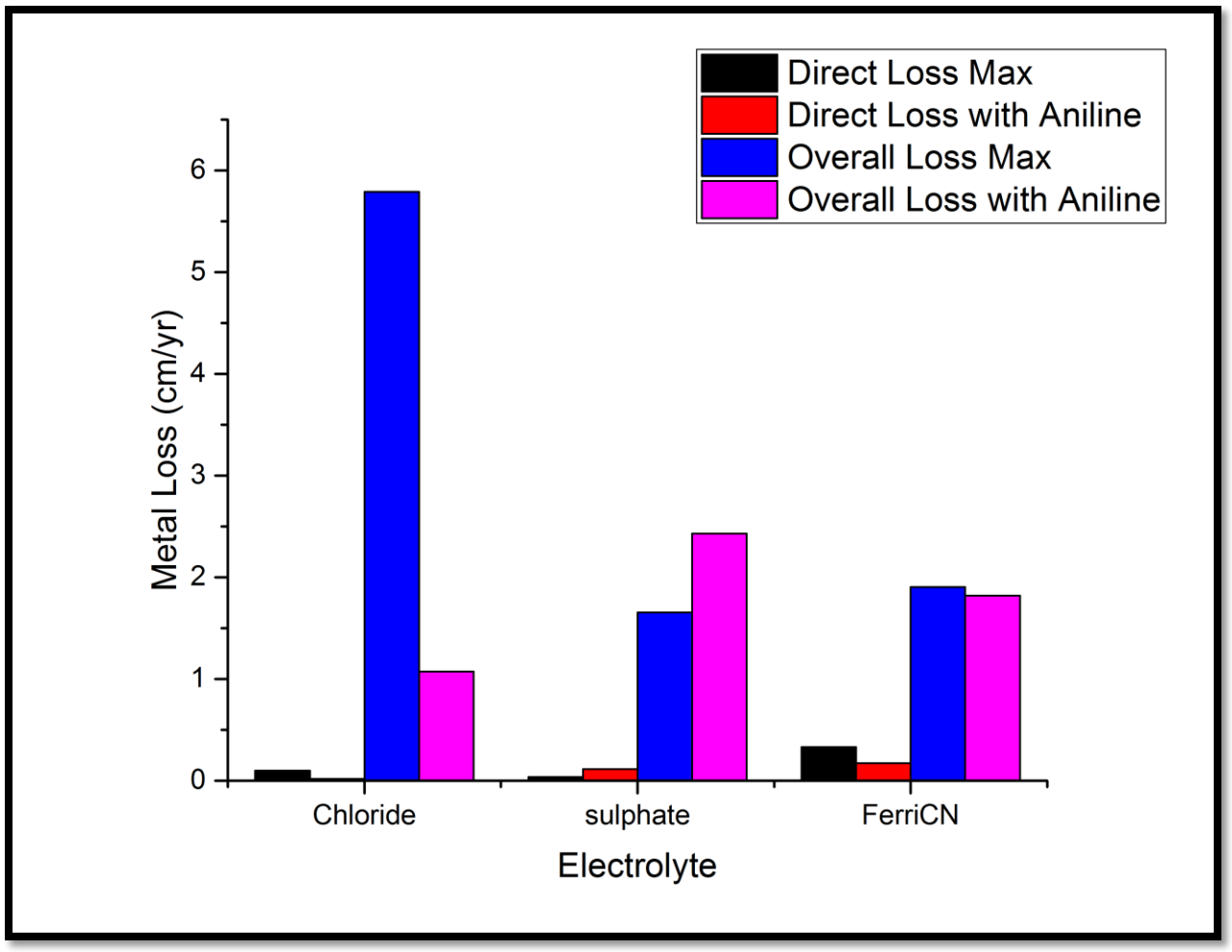


Figure 3.11 Effect of Aniline at maximum concentration in contrast with "Absence of Aniline" at 100˚C.

CHAPTER 4

CONCLUSION

Corrosion is greatly affected by variance in temperature and concentration. With increase in temperature corrosion rates increases rapidly. Chloride, sulphate and Cyanides are very aggressive attackers. In case of chlorides, corrosion increases with increase in concentration and temperature. Table 3.5 enlists the concentration on which maximum corrosion was observed at room temperature. Nitrites have a tendency to form thin and strong films. This was observed in the reduction in corrosion rate when combination of nitrite-sulphate and nitrite-chloride were used as corrosive environment. Film formation plays an important role in inhibition of metal. In general, corrosion inhibition efficiency of film depends upon the strength of scale and thickness of the film. Loosely bounded scales permit the contact of metal with corrosive environment. Aniline is a good corrosion inhibitor. It is most efficient against chlorides and least against Phenols. At high temperature Aniline loses its inhibiting effect and add to corrosion in case of phenols and sulphates. Aniline is effective in inhibition against corrosion due to wastewater.

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APPENDIX I
(Corrosion Rates at Room Temperature)

Chloride:

Concentration (mg/l)	Corrosion Rate in (cm/yr.)
0	0.016216469
5	0.036589552
10	0.074287436
15	0.044645041
25	0.06775849
35	0.08234782
40	0.128460778
50	0.165835055
80	0.060238409
100	0.041323878
125	0.040863168
150	0.042504573
175	0.028323962
200	0.042600377
225	0.037987337

Sulphate:

Concentration (mg/l)	Direct Metal Loss (cm/yr.)	Overall Metal Loss (cm/yr.)
0	0.00896	0.016216
1	0.001896	0.008252
2	0.002825	0.008873
5	0.002019	0.013305
10	0.002852	0.013181
15	0.002516	0.011226
20	0.001573	0.012117
25	0.002074	0.012745
30	0.006464	0.0118

Ferricyanide:

Concentration (mg/l)	Direct Metal Loss (cm/yr.)	Overall Metal Loss (cm/yr.)
0	0.00896	0.016216
1	0.018005	0.040332
2	0.01742	0.029425
4	0.017323	0.033564
8	0.020879	0.043214
16	0.016724	0.038558
24	0.01644	0.033521
32	0.018625	0.035109
40	0.020199	0.045229

APPENDIX II
(Corrosion Rates at 100˚C)

Chloride:

Concentration (mg/l)	Corrosion Rate (cm/yr)
0	1.611653024
2	1.581301069
3	3.543364785
16	1.121416826
32	1.743260311
64	4.899239886
128	4.027368789
256	5.790920299

Sulphate:

Concentration (mg/l)	Direct Metal Loss (cm/yr.)	Overall Metal Loss (cm/yr.)
0	-0.0633	1.611653
1	-0.01029	1.214738
2	-0.09312	0.971303
4	0.022481	1.077499
6	0.036776	1.651966
8	0.020881	0.974963
10	0.077994	1.152244
15	0.23295	1.198488
20	0.062679	1.002868
25	0.102796	1.121265
30	0.137766	0.897801

Ferricyanide:

Concentration (mg/l)	Direct Metal Loss (cm/yr.)	Overall Metal Loss (cm/yr.)
0	0.00896	0.016216
1	0.060855	1.156254
2	0.047591	1.126313
4	0.136987	2.450548
8	0.18275	0.989898
16	0.285932	1.779132
24	0.329884	1.904073
32	0.359475	1.851245
40	0.390478	1.799124

APPENDIX III

(Corrosion rates with Aniline at Room Temperature and 100˚C)

Room Temperature:

Compound	Direct Metal Loss (cm/yr.)	Overall Metal Loss (cm/yr.)
Chloride	0.012885	0.019413
Sulphate	0.001002	0.007245
Ferricyanide	0.009282	0.01976

100˚C:

Compound	Direct Metal Loss (cm/yr)	Overall Metal Loss (cm/yr)
Chloride	0.018731	1.072378
Sulphate	0.113675	2.429388
Ferricyanide	0.173383	1.818256